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**Process for the Production of a Polyester
with a High Degree of Polymerization**

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(54) Title of the Invention: **Process for the Production of a Polyester with a High Degree of Polymerization**

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SPECIFICATION**1. Title of the Invention**

Process for the Production of a Polyester with a High Degree of Polymerization

2. Claims

1. A process for the production of a polyester wherein terephthalic acid, a bifunctional carboxylic acid having terephthalic acid as the main component thereof, or an ester-forming derivative thereof is reacted with ethylene glycol, a glycol having ethylene glycol as the principal component thereof, or an ester-forming derivative to produce a polyester, said method characterized by adding hydrogen chloride in a proportion of $0.2 \times 10^{-4} - 30 \times 10^{-4}$ mol per mole

of the raw material acid component after having substantially completed the esterification or transesterification reaction.

3. Detailed Description of the Invention

(Field of Industrial Utilization)

The present invention relates to a process for the production of a polyester; in particular, to a process for rapidly producing a polyester that has a high degree of polymerization and excellent mechanical and thermal properties.

(Prior Art)

Polyesters, especially polyethylene terephthalate and polyesters having ethylene terephthalate units as the main structural units, are widely used in common practice for fibers, films, and other molded articles because of their many excellent properties.

In the manufacture of polyethylene terephthalate, bis-(β -hydroxyethyl)terephthalate and/or a low-polymer thereof is usually formed by transesterifying dimethyl terephthalate and ethylene glycol or by directly esterifying terephthalic acid and ethylene glycol, and a polyester of the desired properties is then produced by conducting a polycondensation reaction.

However, since the polycondensation step, especially the final polycondensation step, must be conducted at a high temperature of from 280 to 300°C for a long period of time in order to obtain a polyester with an intrinsic viscosity of, for example, 0.6 or higher, the polymer usually turns yellow as a result of thermal decomposition and other secondary reactions, and the increases in the concentration of terminal carboxyl groups and in the content of diethylene glycol bonds have an adverse effect on the physical properties of the polyester.

A catalyst is generally used in the manufacture of polyester. For example, Japanese Kokoku Patent No. Sho 28-4640 mentions the use of hydrogen chloride as an esterification catalyst. However, when hydrogen chloride is added from the time of the esterification reaction, the content of diethylene glycol bonds increases as a result of secondary reactions, its activity as a polycondensation catalyst declines in the extreme, and it becomes impossible to shorten the polycondensation reaction time.

(Object of the Invention)

The object of the present invention is to provide a process for rapidly producing a polyester that has a high degree of polymerization and excellent mechanical and thermal properties.

(Constitution of the Invention)

As a result of research intended to attain the aforementioned object, the present inventors discovered that it is effective to add a prescribed quantity of hydrogen chloride at a prescribed time, and perfected the present invention. In essence, the invention is as follows.

A process for the production of a polyester wherein terephthalic acid, a bifunctional carboxylic acid having terephthalic acid as the main component thereof, or an ester-forming derivative thereof is reacted with ethylene glycol, a glycol having ethylene glycol as the principal component thereof, or an ester-forming derivative to produce a polyester, this method characterized by adding hydrogen chloride in a proportion of $0.2 \times 10^{-4} - 30 \times 10^{-4}$ mol per mole of the raw material acid component after having substantially completed the esterification or transesterification reaction.

The hydrogen chloride in the present invention must be added after the esterification or transesterification reaction has been substantially completed, i.e., when the rate of reaction has reached 90% or higher, and ideally 92-98%. Addition prior to this time causes problems such as those mentioned above.

The amount of hydrogen chloride added must be a proportion of $0.2 \times 10^{-4} - 30 \times 10^{-4}$ mol per mole of the acid component, which is a starting material for the production of the polyester. The addition has essentially no effect when the amount added is lower than this range. Not only does the effect of addition reach saturation, but the polycondensation reaction is also delayed, ordinary stainless steel reactors undergo corrosion, and a special reactor such as a ceramic reactor must be used when the amount added is higher than this range.

The principal acid component in the present invention is terephthalic acid or an ester-forming derivative thereof, such as an alkyl ester or phenyl ester. Part of the acid component (usually less than 30 mol%) may be replaced with one or more compounds selected from among

methyl terephthalic acid, isophthalic acid, methyl isophthalic acid, 5-sodium sulfoisophthalic acid, phthalic acid, diphenyl dicarboxylic acid, diphenylsulfone dicarboxylic acid, diphenoxyethane dicarboxylic acid, naphthalenedicarboxylic acid, adipic acid, sebacic acid, p-hydroxyethoxybenzoic acid, ester-forming derivatives thereof, and the like. On the other hand, the principal glycol component is ethylene glycol or an ester-forming derivative of ethylene glycol, such as ethylene oxide. Part of the glycol component (usually less than 30 mol%) may be replaced by one or more compounds selected from among aliphatic, aromatic, alicyclic, and other diol compounds, such as propylene glycol, tetramethylene glycol, 1,4-cyclohexanedimethanol, 1,4-cyclohexanediol, 1,4-bis-hydroxyethoxy benzene, ester-forming derivatives thereof, and the like.

Any known method can be used to manufacture a polyester from these bifunctional carboxylic acids and glycols. For example, the prescribed properties can be obtained by a method in which bis-(β -hydroxyethyl)terephthalate and/or a low-polymer thereof is formed by transesterifying dimethyl terephthalate and ethylene glycol, directly esterifying terephthalic acid and ethylene glycol, or carrying out an addition reaction of terephthalic acid and ethylene oxide, and in which a polycondensation reaction is then conducted by adding a prescribed quantity of hydrogen chloride. Additives such as catalysts, stabilizers, pigments, dyes, fluorescent whiteners, nucleating agents, polymerization accelerators, lubricants, and bulking agents can be introduced as needed in addition to the hydrogen chloride catalyst after the transesterification or esterification reaction has been substantially completed.

The degree of polymerization of the polyester produced is not especially restricted, but the intrinsic viscosity (abbreviated hereinafter as $[\eta]$) is preferably in the range of 0.6-1.0 because of practical considerations, as determined based on the solution viscosity measured at 20°C after the polyester is dissolved in a mixed solution of phenol and tetrachloroethane (1:1).

The polyester can be manufactured in accordance with the present invention without adding any additives other than the hydrogen chloride catalyst, and a pure polyester devoid of any catalyst residue or the like can be obtained by thoroughly scattering the residual hydrogen chloride in the polyester by extended hot-air drying or vacuum drying at a temperature higher than the usual drying temperature (about 140°C), i.e., usually 160-220°C, and preferably

180-200°C. In addition, the thermal decomposition rate and the decrease in the degree of polymerization are minimized.

(Working Examples)

The present invention is explained concretely below through working examples. However, the present invention is in no way limited by these working examples.

In the working examples, "parts" means "parts by weight," and the characteristics were measured as follows.

(a) The terminal carboxyl group concentration (COOH) was determined by titration with 1/10N potassium hydroxide solution in benzyl alcohol. A lower value is preferred.

(b) The concentration of diethylene glycol bonds (DEG) was determined by a method in which decomposition was performed for two hours under methanol reflux, and an analysis was conducted by gas chromatography. A lower value is usually preferred.

Working Examples and Comparative Examples

Bis(β -hydroxyethyl)terephthalate and low polymers thereof were produced from terephthalic acid and ethylene glycol by a known method. The quantities of hydrogen chloride shown in Table 1 [amount of HCl (mol) per mole of acid component] were added to 100 parts of the above, the temperature was raised to 285°C, the interior of the system was gradually evacuated, and polycondensation was finally carried out at 0.1 mm Hg for the length of time shown in Table 1.

Polyester was also produced in the same way using antimony trioxide in an amount of 2×10^{-4} mol/mol of acid component instead of the hydrogen chloride as the catalyst (reference example).

Table 1 shows the characteristics of the polyesters obtained.

Table 1

	Polycondensation time (min)	Amount of catalyst added		Properties of polyester produced		
		HCl (mol)	(parts)	$[\eta]$	DEG (mol%)	COOH (Eq/ton)
Working example 1	120	10×10^{-4}	0.055	0.88	1.67	18.3
Working example 2	180	2×10^{-4}	0.011	1.00	2.24	16.7
Comparative example 1	120	0.1×10^{-4}	0.006	0.19	1.94	68.4
Comparative example 2	120	40×10^{-4}	0.22	0.78	3.77	19.2
Comparative example 3	120	70×10^{-4}	0.35	0.46	4.32	14.6
Reference example	120	—	—	0.68	1.85	15.0

Furthermore, the amount of residual hydrogen chloride in the dry polyester obtained in Working Example 1 was below the limit of detection (30 ppm) by fluorescence x-ray analysis.

The degree of polymerization did not increase and the stainless steel reactor was severely corroded in Comparative Example 3, where a large amount of hydrogen chloride was added.

(Merits of the Invention)

As has been described above, the method of the present invention makes it possible to manufacture polyester with a high degree of polymerization and excellent mechanical and thermal properties in a short time. In particular, it is possible to prevent increases in the content of terminal carboxyl groups and diethylene glycol bonds in the polyester produced in the treatment step that accompanies or follows the polycondensation reaction, and to greatly improve product quality when the polyester is used for fibers, films, and other molded articles.

It is also possible to obtain pure polyester that contains no catalyst residues or the like if the polyester is manufactured without adding any additives other than hydrogen chloride.

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